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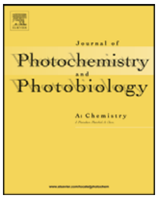

Nanolayers of selected porphyrin and phthalocyanine dyes on solid substrates studied by electronic absorption and IR reflection–absorption spectroscopy

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ABSTRACT

Electronic absorption and IR reflection–absorption spectra in non-polarized and in polarized light for lead porphyrin as well as magnesium and lead phthalocyanine dyes when deposited in the form of Langmuir–Blodgett (LB) nanolayers on solid inorganic surfaces (quartz, semiconductor and metal) were measured. Some IR bands of the Langmuir–Blodgett dye layers' spectra show frequency shifts and changes in the relative intensities as well as in half widths when compared with the vibrational features of powdered dyes dispersed in KBr pellets, which were used as references. The FT-IR spectroscopic examination of the Langmuir–Blodgett layers allowed to estimate electron redistribution at the interface between dye layer and solid substrates. The Langmuir–Blodgett films of different thicknesses (3, 5, 10 layers) were studied at various angles of IR beam incidence and different light polarizations. The most spectacular results were obtained for the grazing incidence (80°) and films of 5 layers for dyes on the Au substrate. The IR spectroscopy was supported with electronic absorption studies (UV–vis) to follow interaction at interface between the dye layers and the substrates as well as to evaluate linear dichroism and to determine arrangement of molecules in the Langmuir–Blodgett films. Molecular arrangement in the Langmuir–Blodgett layers was discussed. It was shown that the dye molecular planes are rather randomly oriented in the Langmuir–Blodgett films with a tendency that the Q_y and Q_x transition moments in the phthalocyanine macroring are slightly directed along the y-axis (Langmuir–Blodgett dipping direction) and the x-axis direction, respectively.

1. Introduction

Porphyrin and phthalocyanine dyes are interesting objects of numerous investigations in last decades, because they are perfect agents in processes of light energy conversion as for example in modelling of photosynthesis, in organic electronics and photonics, in photodynamic therapy of cancer, and other fields [1–5]. Semiconducting properties of organic dye layers have initiated testing of systems that can be tailored to construct optoelectronic and molecular photonic devices such as, e.g. organic light emitting diodes and dye-sensitized solar cells [6,7].

In optoelectronic and photovoltaic devices organic dyes are in direct contact with metal or inorganic surfaces and interfacial effects are involved in interaction processes occurring between dye thin layer and solid. The crucial points in searching for good quality of optoelectronic and photonic devices are effective electron transfer processes in dye layers as well as proper molecular arrangement at the interface of dye layer–solid substrate.

The FT-IR spectroscopy is a very valuable method for investigating surface molecular films and it does not yield any damage to the layer. The shape, intensity and position of IR bands are sensitive to the structure and conformation of various functional groups of molecules in molecular layers as well as to their interaction with a substrate. Additionally, since the IR absorption depends on an angle between the direction of IR beam (and also its polarization) and on the transition moment of a given molecular vibration, it is possible to estimate orientation of molecules in layers.

A variety of IR spectroscopic methods has been applied for investigations of LB films on various substrates. Especially powerful technique is the IR reflection–absorption spectroscopy (IRRAS) of films deposited on a strongly reflecting metal substrate [8–12]. The IRRS spectroscopy was also used for studies of LB films on non-metallic substrates, such as glass or semiconductor [13–17]. Transmission measurement in combination with IRRAS spectroscopy on metal at grazing incidence is a very good method for quantitative analysis of molecular orientation [8,9,17]. Non-metal substrates exhibit lower reflectivity in comparison with metal and, moreover, the electric

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vectors at the interface substrate–organic film are present in three directions, what complicates the interpretation of the recorded IR spectra. Thus we have also focused our attention on electronic absorption examinations to get insight into interfacial spectroscopic effects on the dye layer–inorganic substrate.

In our previous papers, we have presented the results of a study of porphyrin and phthalocyanine bulk systems and their ability for photoactivity in photovoltaics [18–21] and we also focused our attention on morphology and topography of the porphyrin/phthalocyanine Langmuir–Blodgett (LB) layers on solid substrates [22]. Formerly, we also presented preliminary investigations of the vibrational features of porphyrin and phthalocyanine dyes in solutions and in LB layers [23]. In this paper, we extend our study and characterize the LB layers prepared with selected porphyrin and phthalocyanines on different substrates (metal, semiconductor and insulator). We present here electronic absorption (UV–vis) and reflection–absorption (IR) spectra obtained with either non-polarized or polarized light in two aspects: (i) to follow interaction at the interface organic dye–inorganic substrate and modification of electron distribution in the LB systems due to interfacial interaction between dyes and substrates, and (ii) evaluation of linear dichroism and of dye arrangement in the LB layers. For this purpose the UV–vis and infrared (IR) spectroscopy seem to be very good tools. The measurements have been done for different angles of incidence, various numbers of layers and different light polarizations.

The results presented in this paper and knowledge on interaction between the thin molecular layer and solid substrate as well as on molecular arrangement of the dyes in the thin layer are essential in seeking for good molecular agents for molecular optoelectronics and photovoltaics.

2. Materials and methods

2.1. Dyes and substrates

Three dyes were investigated: two phthalocyanines complexed with magnesium (MgPc) or lead (PbPc) and one tetraphenyl porphyrin complexed with lead (PbTPP). Their molecular structures are presented in Fig. 1. The dyes MgPc, PbPc and PbTPP were purchased from Aldrich and Porphyrin System (Germany) and used without further purification. Three solid substrates for LB layers were used: gold on glass plate (Au), In_2O_3 on quartz plate and quartz plate.

2.2. Preparation of Langmuir–Blodgett films

Preparation of LB layers was performed by the use of a KSV 2000 minitrough (KSV Instruments Ltd., Finland) equipped with a temperature control system. The Langmuir trough area was 380 mm × 90 mm. Temperature of subphase was kept constant (22 °C) with a cooling circulator. The subphase was deionized water (electrical resistivity 18.2 MΩm) obtained with a Mili-Q water purification system (Milipore Corp., Austria). The samples were dissolved in chloroform (MgPc and PbTPP) and dimethylsulfoxide/chloroform (1:4 v/v) (PbPc) and 10^{-4} M solutions were spread onto the subphase and then let chloroform to be evaporated (15 min). The floating film of a Langmuir layer was compressed symmetrically from both sides with the motion barrier speed of 3 mm/min.

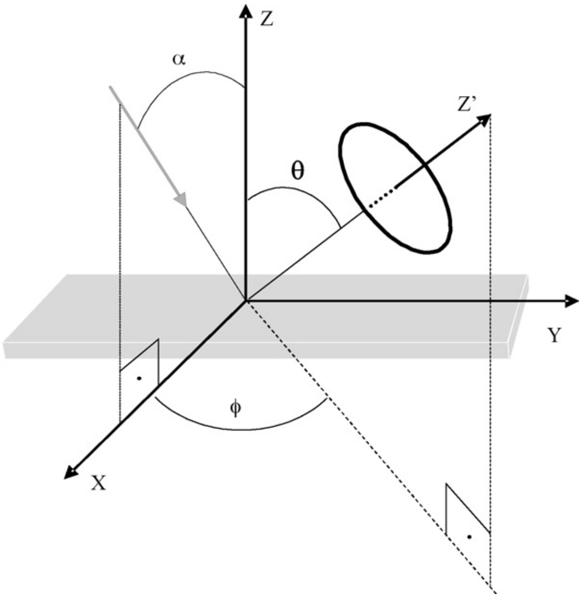

Fig. 2. Scheme of the laboratory (x, y, z) and molecular systems (z', θ, ϕ), x–y: plane of the LB film, y: dipping LB layer direction, z: normal to the LB layers, z': normal to the dye molecular plane, α: angle of light beam incidence, θ: angle between z and z' axes, 90°-ϕ: angle between the projection of normal z' and LB director (y).

The molecular films were deposited on the substrates by the Langmuir–Blodgett method. The Y-axis of the film (Fig. 2) represents the direction of the film deposition by an upstroke and a downstroke.

The transfer of molecular layers was done onto hydrophilic Au, In_2O_3 or quartz at the surface pressure of 18 mN/m (samples: MgPc, PbPc), 13 mN/m (sample PbTPP), with the speed of 2 mm/min. The number of layers was 3–10 depending on the sample and substrate.

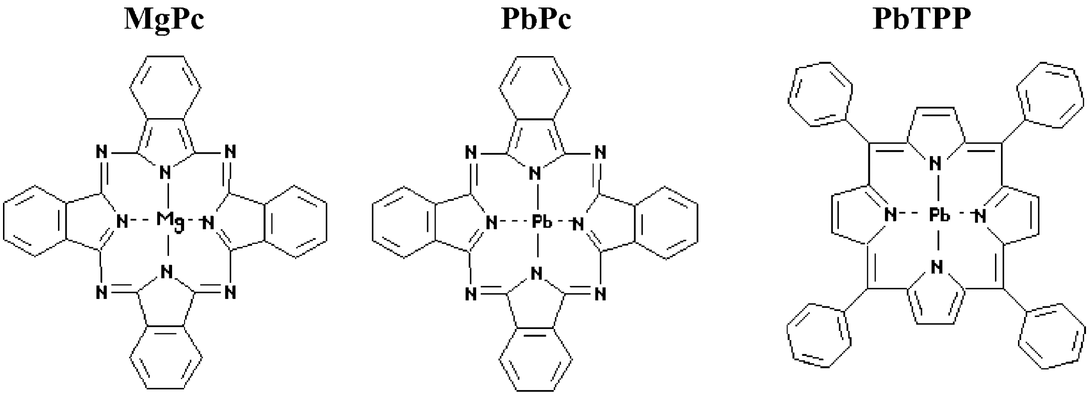

Fig. 1. Molecular structures of MgPc, PbPc and PbTPP.

2.3. Infrared spectroscopy

FT-IR absorption and reflection–absorption spectra were recorded at room temperature using a FT-IR Bruker spectrometer Equinox 55 equipped with a reflection insert especially designed for thin film measurements at various angles of incidence (20°–80°). All measurements were done with the samples of various thicknesses (3, 5, 10 layers) and performed with 4 cm^{-1} resolution in the range of 400–4000 cm^{-1}. However, in the paper we show only 700–1400 cm^{-1} region as the most interesting for porphyrin and phthalocyanine dyes. For measurements in polarized light the IR beam was polarized with a golden wire grid deposited on an AgBr plate. The IR reflectance of the substrates without LB films was measured as references. The results obtained for dyes in the LB layers are compared with those in the KBr pellets. The number of interferogram accumulations was between 150 and 300. The IR band parameters (band position, half width and band intensity) were determined from the spectra with the Peak-Fit programme.

For vibrational analysis of LB films in the experiments in polarized light reflection–absorption method was applied with electric vector of the incident beam either parallel (p-polarization) or perpendicular (s-polarization) to the plane of incidence.

2.4. Linear dichroism in the UV–vis light

The electronic absorption spectra of the dye LB films were recorded using a double beam spectrophotometer Carry 4000 (Varian) in the range from 350 to 900 nm for 5 or 10 layers of the dyes in non-polarized and polarized light. Polarized spectra were measured at the angle α equal to 0°, 30° and 50° (α-angle between light beam and the normal to the dye layer plane) (Fig. 2).

3. Results and discussion

3.1. Infrared examinations

In the first stage of the paper we focus on the spectral characteristics of the dye LB films. Fig. 3 shows the FT-IR reflection–absorption spectra recorded at the angle of incidence 80° in the range from 700 to 1400 cm^{-1} for 5 layer films on various substrates. The IRRAS spectra are presented together with the absorption spectra of powdered compounds dispersed in the KBr pellet. Although many interferograms were accumulated for films deposited on the quartz substrate, their IRRAS spectra are of much worse quality in comparison with the analogous spectra of films on Au and In_2O_3. The most important IR bands, observed in the absorption spectra of dyes in KBr, are gathered and assigned in Table 1, while the IR bands of thin films are analysed in Table 2. For MgPc on Au the strongest vibrational bands are registered at 1064, 1097, 1130, 1165, 1284 and 1333 cm^{-1}, whereas for PbPc on Au these peaks are slightly shifted and arrived at 1061, 1090, 1114, 1163, 1288, 1340 cm^{-1}, respectively [23,24]. For PbTPP the strongest bands at 716 and 802 cm^{-1} are observed. In comparison with the spectra of the dyes in KBr the vibrational bands of LB films are shifted towards higher frequencies (up to 16 cm^{-1}) and their relative intensities are altered. We assume that these modifications can be assigned to an interaction between metallic substrate and dye layer, i.e. to a small charge transfer at the substrate–layer interface.

The most spectacular changes are noticed for MgPc on Au in the range of 1050–1200 cm^{-1} and 1330–1350 cm^{-1}. Thus in the discussion we focus our attention on Fig. 3(A) as an example. The bands with a doublet structure are seen in the range from about 1050 to 1130 cm^{-1} [23,24]. The splitting could be related to a modification of the electronic density on molecules

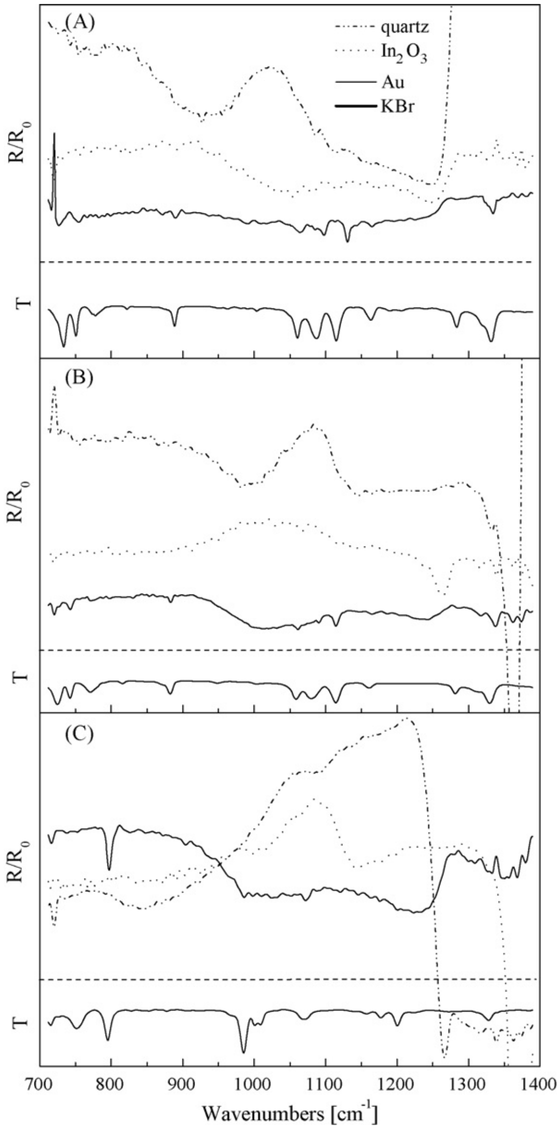

Fig. 3. Reflection–absorption IR spectra for 5 layers of MgPc (A), PbPc (B) and PbTPP (C) on different substrates (quartz, In_2O_3, Au); the angle of incidence −80°; the transmittance spectra in KBr pallet are also shown.

Table 1
Most important vibrational bands of the dyes dispersed in KBr; vs-very strong, s-strong, m-middle, w-weak

ω [cm^{-1}]			Approximate assignment
MgPc	PbPc	PbTPP	
733 vs	724 vs	715 m	Mainly C–H bending out-of-plane
751 s	742 s	765 m	
778 m	770 m	800 s	
888 s	882 s	877 vw	
		985 vs	
		995 m	
1003 w	1002 w	1001 vs	Mainly C–H bending in-plane
1060 s	1058 s	1070 m	
1087 s	1079 s		
1114 vs	1114 vs		
1163 s	1161 s		
1283 s	1282 s		
1332 vs	1330 vs	1328 m	C–N stretching

Table 2
IR band parameters of the dyes in KBr and their LB films on Au and In_2O_3

KBr		Au			In_2O_3		
ω [cm^{-1}]	$\Delta\nu_{1/2}$ [cm^{-1}]	ω [cm^{-1}]	$\Delta\nu_{1/2}$ [cm^{-1}]	Shift	ω [cm^{-1}]	$\Delta\nu_{1/2}$ [cm^{-1}]	Shift
MgPc							
1060	14	1064	10	4+			
1087	21	1097	8	10+	1082	10	5−
1114	15	1130	7	16+			
1163		1165		2+			
1283		1284		1+	1284	8	1+
1332	14	1333	9	1+	1340	6	8+
PbPc							
1058		1061		3+			
1079		1090		11+			
1114	14	1114	9	0			
1161		1163		2+			
1282		1288		6+			
1330	16	1340	8	10+	1339	6	9+
PbTPP							
715		716		1+	719		4+
800	10	802	8	2+			

as a result of deposition of the dyes on a substrate, due to an interaction with solid Au. The electron density changes were discussed also in our previous paper [23] and related to a possibility of electron transfer between solid substrate and dye, which can explain the modification of IR spectra of dyes in the LB layers with regard to those in the KBr pellet. It is known that a weak covalent bonding usually exists between a thin dye layer and metallic substrate. A possibility of existence of a small permanent polarization at the substrate/layer interface and its influence on IR spectra should be also taken into account. The band splitting for the MgPc on the In_2O_3 substrate is less markedly seen. Thus the differences between the dye films on the Au, In_2O_3 and quartz substrates could be related to various electron densities in layers on Au in comparison with those on In_2O_3 and quartz. The surface morphology of substrate is able to influence the spectra [22] and it can also be a reason of the observed spectral modifications. It is important that in most cases, the bands observed in LB layers are shifted towards higher frequencies; the only exception is the band 1082 cm^{-1} for MgPc on In_2O_3. In general, we can suppose that the observed spectral changes are connected with interaction of the dye molecules with the solid substrates (Au, In_2O_3) and are due to a modification in electron distribution in the dye molecular frame. The interfacial effects should be mainly limited to the first monolayer of dyes on substrate; however, because of semiconducting properties of Mg Pc films [1] one can suppose that the charge is delocalized over whole LB film.

For all substrates (Au, In_2O_3, quartz) the IR bands are superimposed on background, which is not flat and, moreover, it exhibits slight differences for measured spectra. These differences are due to small non-equivalencies between the sample and reference substrates. All the substrates were prepared very carefully by deposition of Au or In_2O_3 on glass plates; nevertheless, small differences are unavoidable, manifesting themselves in IRRAS spectra as very broad either positive or negative bumps in background, but they can be easily identified and subtracted from vibrational bands of LB films.

The vibrational bands of the dye LB films on In_2O_3 substrate are much weaker in comparison with those on Au substrate, therefore, only the strongest bands were detected. In the case of In_2O_3, similarly as for Au substrate, differences between reflectance for various backgrounds are also observed. The imaginary part of the complex refractive index of In_2O_3 is quite large, therefore, depending on the direction of a transition moment, polarization of IR beam, and angle of incidence, negative or positive IR absorption bands with changes of their sign near Brewster angle can be expected [9,13]. Subsequently, we mainly focus our attention on the IR spectra of films on Au.

The non-polarized IRRAS spectra of 5 LB layers of the MgPc and PbPc films on Au substrate recorded at various angles of incidence and in the region of strong vibrational bands are shown in Fig. 4 (A and B), respectively. In agreement to the specific features of reflection from metal surface, the band intensity grows with angle of incidence approaching the largest value at 80°. Such results are expected for reflectance coming from the thin layers on conducting material. However, we observe a discrepancy from the linearity of

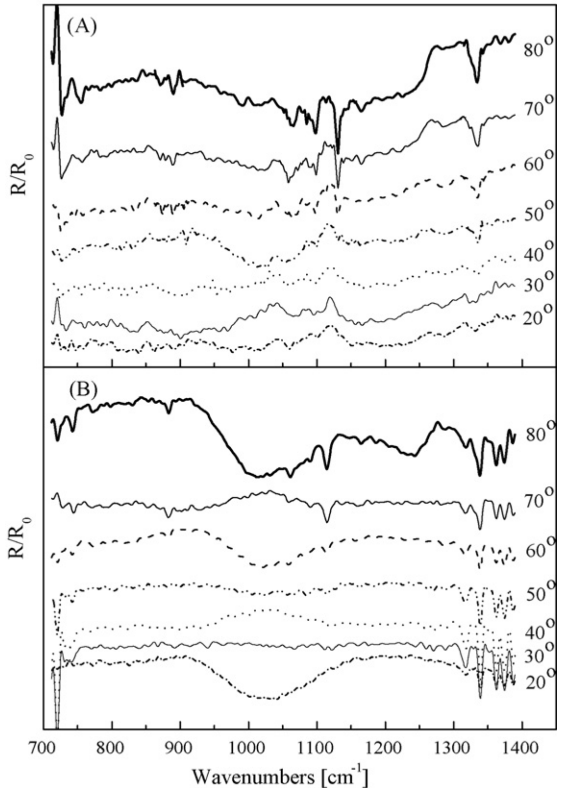

Fig. 4. Reflection–absorption IR spectra for 5 layers of LB films of MgPc (A) and PbPc (B) on Au at various angles of incidence.

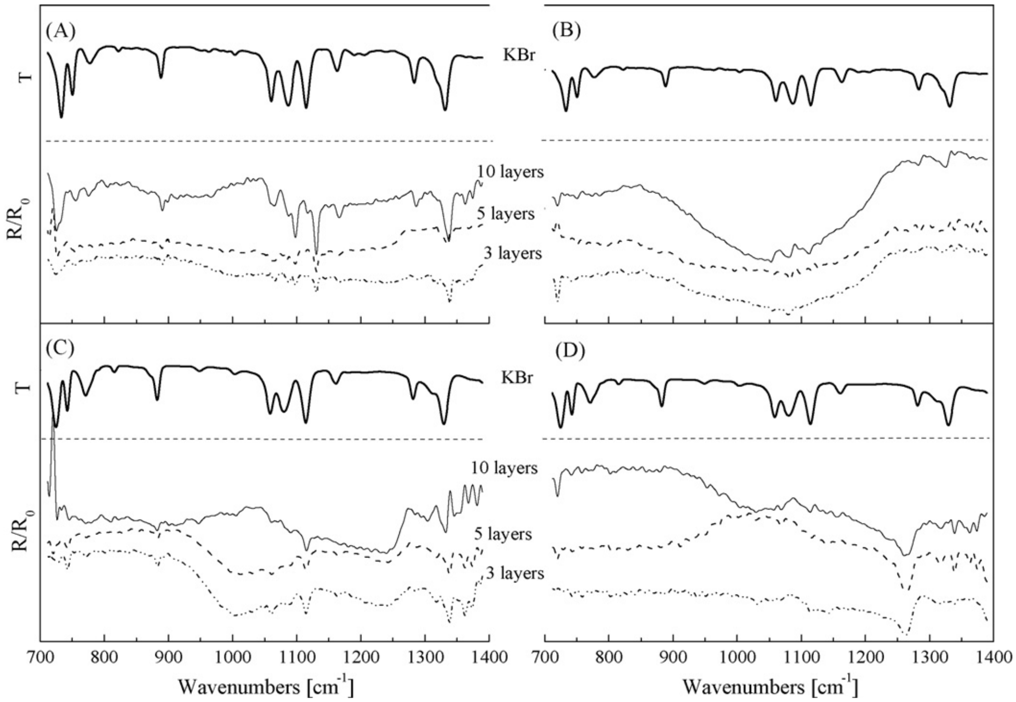

Fig. 5. Reflection–absorption spectra for 3, 5 and 10 layers of LB films of MgPc and PbPc on Au (A and C, respectively) and on In_2O_3 (B and D, respectively) at the angle of incidence 80° (spectra in KBr are also displayed).

the reflectance signal as a function of the angle of incidence (not shown). This discrepancy is due to the specific reflectance from the ultrathin dye layers, on one hand, and could result in a small anisotropy of the layers owing to some orientations of the dyes with respect to the solid surface on the other hand. The last supposition is shown in our preliminary IR experiments done for the dyes examined in polarized light (not shown); in the p: polarized spectra the discrepancy from linearity (at the angle of about 50°) could indicate some orientation of the dyes in the LB films.

In Fig. 5, we display the IRRAS spectra obtained in non-polarized light at the angle of incidence of 80° within the region of the strongest vibrational bands for 3, 5 and 10 LB layers of phthalocyanine dyes (MgPc, PbPc) on the Au or In_2O_3 substrates. The PbTPP and PbPc give very poor signals and therefore we focus our discussion on MgPc. In most cases the signal intensity increases with number of the LB layers, as expected. The band details are clearly seen for the 5 and 10 layers and thus in the polarized light examination we consider 5 and 10 layered films.

It is important to mention about a possibility of aggregation processes for closely packed dyes in LB films. The shape of electronic absorption spectrum of phthalocyanine is found in the paper [1] and discussed in the paper [25]. When monomers are present in a sample the small band at about 608 nm and strong band at about 682 nm are well seen. Otherwise, when dimers are created the huge band arrives at 624 nm [25]. In our absorption spectrum of MgPc in solution the maximum is observed at 609 and 673 nm with hump at 645 nm, indicating that monomers predominate. In LB films on In_2O_3 and quartz the bands at about 609–618 nm arrive, respectively, which could indicate that some modest aggregates appear. If we have aggregates the much stronger band at 608–609 nm should be observed. However, it is not a case for our sample in solution. Thus the small band shift at 609 nm is rather connected with interaction with the substrates. Moreover, the shift of the huge band at 673 nm to 829–833 nm is seen. On the basis of our electronic absorption experiments we can also believe that there is no demetalation and degradation of our dyes.

Obviously, the shapes of IR bands, their frequencies as well as splitting, which are observed in the regions of the porphyrin modes, can have a source in aggregated dye moieties. However, the "red" shifts of the dye absorption spectra are very marked; thus we have every reason to believe that the shifts are predominantly due to the strong dye interaction with the solid substrate [22]. Also the intensity ratios are altered in the dye LB layer when compared to data in KBr. For example, for MgPc the band intensity ratios are found to be 1.1 (1114/1060 cm^{-1}) and 1.4 (1130/1064 cm^{-1}) in KBr and the LB layers, respectively; and for PbPc they are 1.1 and 2.3 in KBr and in the LB layers, respectively. The UV–vis and IR changes in spectra could indicate dye–substrate interaction and dye–dye interaction. Therefore, we can suppose that the aggregated structure formation can contribute to observed dye features in the films. Thus we can believe that the changes in absorption spectra for phthalocyanine on the substrate are predominantly caused by interaction with the solid and the contribution of aggregates is rather small. The observed changes in the IR spectra upon LB film deposition should be also attributed to different dye transient moment orientation in the layer.

3.2. *Molecular arrangement study*

In our IR experiments in polarized light we have used the Au substrate for film deposition since this substrate is the best one among the others used in this paper in reflection–absorption examinations. As mentioned above the IRRAS spectrum of the dye LB film on a metal surface is strongly dependent on light polarization of beam. In IR study, we put our attention on the modes located in the range of 1050–1150 cm^{-1} and at about 1330 cm^{-1}. In Fig. 6, we show the spectra of MgPc and PbPc on Au for two polarizations of incident beams (p and s). The figures evidently show the bands for p-polarization where $\vec{E}$ light vector lies in plane of incidence; for s-polarization the bands are hardly seen, as expected [15]. The intensive p-polarized IR bands are found for example for C–N stretching modes (MgPc on Au: 1333 cm^{-1}, PbPc on Au: 1340 cm^{-1})

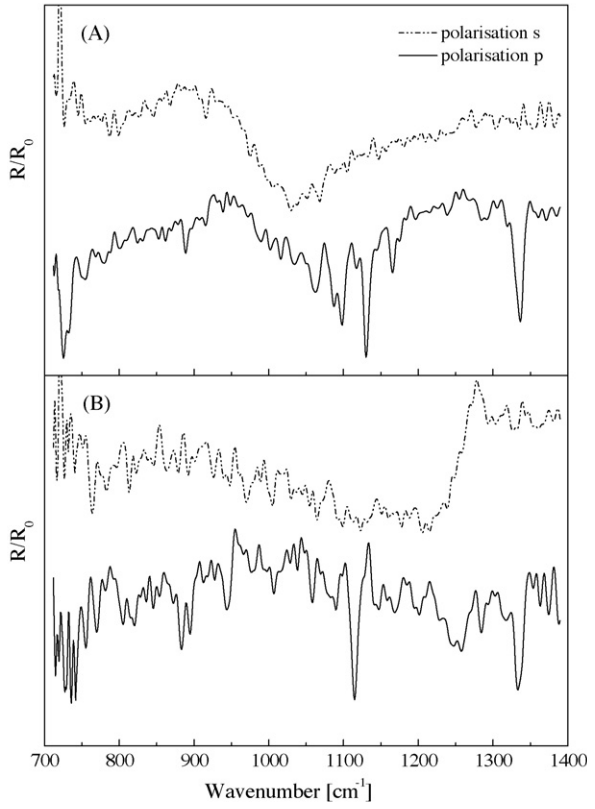

Fig. 6. Polarized reflection–absorption IR spectra for 10 layers of LB films of MgPc (A) and PbPc (B) on Au at the angle of incidence 80°; dashed line: s-polarization, solid line: p-polarization.

and bending in plane C–H modes (MgPc on Au: 1130 cm^{-1}, PbPc on Au: 1114 cm^{-1}).

Molecular arrangement can be evaluated from the polarized light experiments in the visible range. For examinations in the Vis region the molecules were deposited on quartz and In_2O_3 (these substrates are more suitable for the measurements in the visible than Au). One can assume that the molecular arrangement inside films deposited on various substrates is similar. Fig. 7 shows the non-polarized electronic absorption spectra for MgPc (as an example) with the strong Soret band in the blue region (360 nm) and marked Q_x (697 nm) and Q_y (833 nm) bands in the red region. As seen in the figure both the Soret and the long-wavelength bands are strongly shifted towards the "red" region confirming again strong interaction of dyes with the substrate.

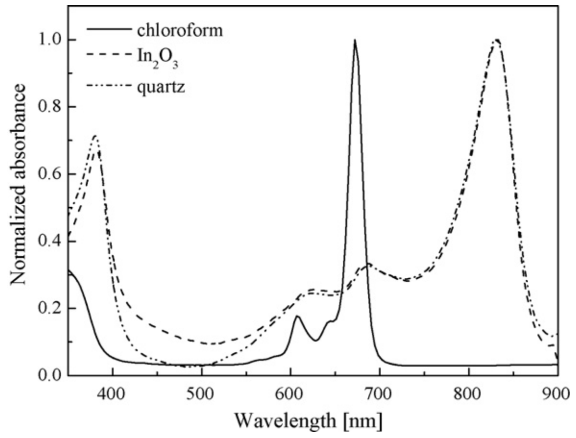

Fig. 7. Normalized to unity electronic absorption spectra of MgPc in chloroform and non-polarized spectra for 5 LB layers deposited on In_2O_3 and quartz.

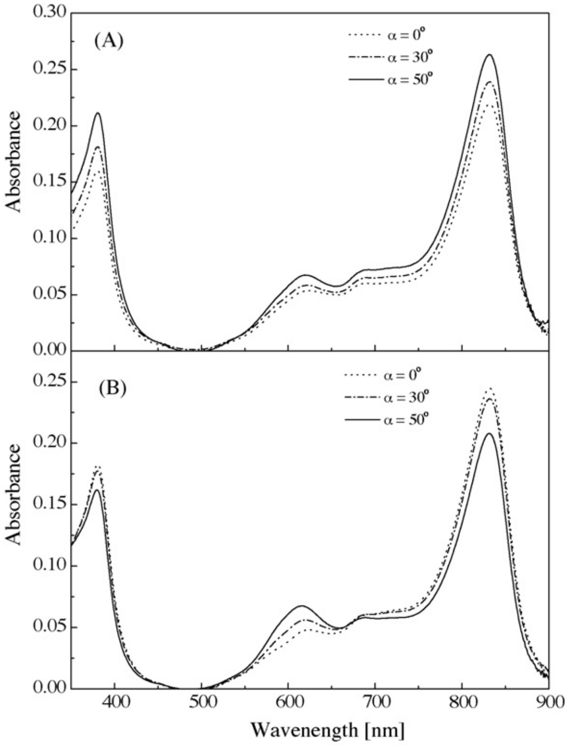

Fig. 8. Polarized electronic absorption spectra for 5 LB layers of MgPc on quartz at different angles of incidence; A and B: $\bar{E}$ perpendicular and parallel to the director, respectively.

In order to evaluate molecular arrangement, absorption measurements in the polarized light were performed at different angles (α) of incidence (Fig. 2). The polarized absorption spectra of the dyes (5 layers) are shown in Fig. 8 (A and B). Under supposition of the flat π–π* molecular structure of the dyes and that the dye layer is illuminated with the polarized light at an angle α, dichroism of the film can be expressed in accordance with [26,27] as:

$$D_\alpha = \left(\frac{A_1}{A_2}\right), \tag{1}$$

where A_1 and A_2 are the dye film absorbances for polarized light with electric vector parallel and perpendicular to the film dipping direction, respectively, with statistical averages:

$$\begin{aligned} \langle\cos^2\theta\rangle &= \frac{D_0-(1+D_0\sin^2\alpha')D_\alpha}{(1-2\sin^2\alpha')D_\alpha-(1+D_\alpha\sin^2\alpha')D_0}, \\ \langle\sin^2\theta\cos^2\phi\rangle &= \frac{D_0-\langle\cos^2\theta\rangle}{1+D_0}. \end{aligned} \tag{2}$$

The meanings of angles θ and φ are described in Fig. 2. The α' is an angle in the film evaluated in accordance with Yoneyama [27]. Experimentally, D_0 and D_α are evaluated on the basis of the polarized absorption experiments for two α's: 0° and α # 0° (30° or 50°), respectively. On the basis of the absorption experiments one can also evaluate a fraction of molecules tilted to the x- or y-axis [27]:

$$F = \frac{\langle\sin^2\theta\cos^2\phi\rangle}{(1-\langle\cos^2\theta\rangle)}. \tag{3}$$

The values of the dichroic ratios D_α, angles θ and φ evaluated from Eqs. (1) and (2) are gathered in Table 3 for MgPc and PbTPP deposited on quartz or In_2O_3. As seen, the θ values and azimuth of φ (expressed as the averages: Eq. (2)) for transition moments

Table 3
Dichroic ratio parameters for MgPc on quartz and In_2O_3 and PbTPP on quartz

Sample	α	D_α	$\langle\cos^2\theta\rangle$	$\langle\sin^2\theta\cos^2\varphi\rangle$	F (±0.02)
MgPc 5 layers on quartz (Q_x band)	0	1.11			
	30	1.04	0.21	0.43	0.54
	50	0.99	0.25	0.41	0.54
MgPc 5 layers on quartz (Q_y band)	0	0.89			
	30	1.0	0.64	0.13	0.37
	50	1.27	0.58	0.16	0.39
MgPc 10 layers on In_2O_3 (Q_x band)	0	1.0			
	30	0.97	0.28	0.36	0.50
	50	0.92	0.27	0.37	0.50
MgPc 10 layers on In_2O_3 (Q_y band)	0	0.96			
	30	1.1	0.59	0.19	0.46
	50	1.32	0.54	0.21	0.47
PbTPP 5 layers on quartz (Soret band)	0	1.03			
	30	1.15	0.50	0.26	0.52
	50	1.54	0.58	0.22	0.53

Q_x and Q_y electronic absorption transition moments in the dye molecular structure responsible for absorption transition at 697 and 833 nm, respectively.

Q_x or Q_y differ only slightly one from another when measured at a different angle α. It is evident that the plane of the MgPc and PbTPP molecules is rather randomly oriented in the plane of the dye layer.

However, the values of F parameters (Eq. (3)) ranged from 0.37 to 0.54 provide an evidence that the dye molecular frame is oriented at about 45° with respect to x- and y-axis. The $\langle\cos^2\theta\rangle$ value which is near 2/3 indicates rather random distribution of transition moments without any specific orientation with respect to the dipping direction in the films. The porphyrins and phthalocyanines are molecules of high molecular symmetry (D_{4h}) and thus resulting in the F values nearly to 0.5. However, for the Q_y transition moment in MgPc the F values range between 0.37 and 0.47 (it means <0.5) whereas for the Q_x transition moments the F values lie in between 0.50 and 0.54 (it means $\geq$0.5). Thus these results suggest that the MgPc molecules show a tendency to be slightly oriented with the Q_y along the dipping direction of the monolayer. In contrast to the Q_y transition moment, the MgPc Q_x is rather faced preferable to the x-axis. Our results differ from those described by other authors for copper phthalocyanines [27]; the main reason of this dissimilarity is the fact that copper phthalocyanine is asymmetric and this asymmetry can lead to different distributions.

Moreover, the dichroic data (Table 3) for 5 and 10 dye's layers proof that the porphyrin and phthalocyanine dyes in consecutive layers tend to be oriented in a similar way.

Under supposition of the flat porphyrin and porphyrazine macro-rings and the perpendicular orientation of the Q_y transition moment with respect to the Q_x as well as taking into account the values of F parameters, θ′s and ϕ′s averages and the results of the polarized absorption data, we can state that the Q_y and Q_x transition moments in the phthalocyanine ring are slightly directed along the y-axis (LB film dipping direction) and x-axis directions, respectively.

4. Conclusions

In the paper, we have mainly focused on interaction between porphyrin or phthalocyanine dyes and solid substrates as well as molecular arrangement in LB films.

Using IR and UV–vis spectroscopy we have followed the interaction of the MgPc and PbTPP thin layers with the inorganic solid substrate which leads to an interfacial electron redistribution. The study of molecular arrangement in the LB layers shows that the MgPc and PbTPP are rather randomly arranged in the dye layer showing tendency to be slightly oriented with their Q_y transitions along the dipping direction in the film. Moreover, it was shown that molecular arrangement of the dyes in the thin LB layers is kept up to ten layers at least.

The results obtained for the MgPc and PbTPP in LB nanolayers seem to be essential in understanding of interfacial spectroscopic processes occurring in organic solid materials deposited on inorganic solid substrates and thus important for further developing of photovoltaics and optoelectronic devices.

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